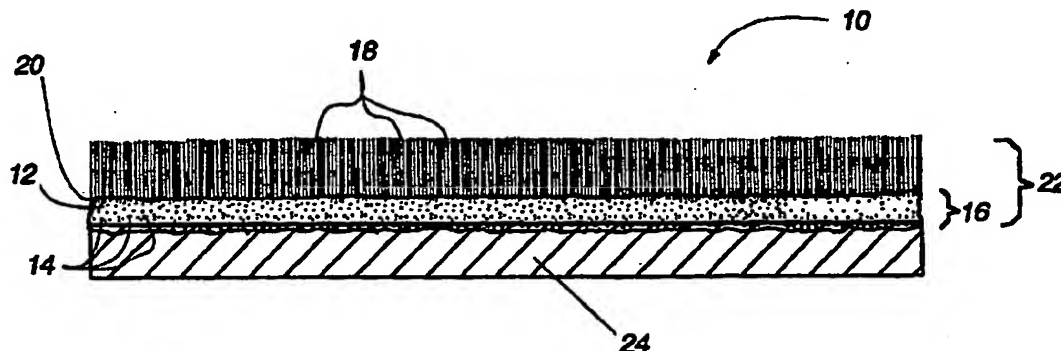




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09K 3/18, 3/20, B32B 19/04		A1	(11) International Publication Number: WO 95/34609
			(43) International Publication Date: 21 December 1995 (21.12.95)
(21) International Application Number: PCT/US95/07467		(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LT, LV, MD, MG, MN, MX, NO, NZ, PL, RO, RU, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(22) International Filing Date: 13 June 1995 (13.06.95)			
(30) Priority Data:			
08/259,964	14 June 1994 (14.06.94) US		
08/477,824	7 June 1995 (07.06.95) US		
(71) Applicants: GATEWAY TECHNOLOGIES, INC. [US/US]; Suite 200, 6680 Gunpark Drive, Boulder, CA 80301 (US). R.H. WYNER ASSOCIATES, INC. [US/US]; 208 Manley Street, West Bridgewater, MA 02379 (US).			
(72) Inventors: ZUCKERMAN, Joseph, L.; 56 Hickory Place, Livingston, NJ 07039 (US). PERRY, Bernard, T.; 5760 Slick Rock Court, Boulder, CO 80301 (US). PUSHAW, Robert, J.; 106 Terra Alta Circle, Havertown, PA 19083 (US). WYNER, Daniel, M.; 67 Central Pike, North Scituate, RI 02857 (US).			
(74) Agents: BURTON, Carol, W. et al.; Holland & Hart, P.O. Box 8749, Denver, CO 80201-8749 (US).			

(54) Title: ENERGY ABSORBING FABRIC COATING AND MANUFACTURING METHOD



(57) Abstract

A coating composition for fabrics includes wetted microspheres containing a phase change material dispersed throughout a polymer binder, a surfactant, a dispersant, an antifoam agent and a thickener. Preferred phase change materials include paraffinic hydrocarbons. The microspheres may be microencapsulated. To prepare the coating composition, microspheres containing phase change material are wetted and dispersed in a dispersion in a water solution containing a surfactant, a dispersant, an antifoam agent and a polymer mixture. The coating is then applied to a fabric. In an alternative embodiment, an extensible fabric (24) is coated with an extensible binder (12) containing microencapsulated phase change material (14) to form an extensible, coated fabric (10). The coated fabric (10) is optionally flocked with fibers (18). The coated, extensible fabrics are manufactured using transfer techniques.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

5

ENERGY ABSORBING FABRIC COATING AND MANUFACTURING METHOD

Field of the Invention

This invention relates to substrate coatings containing energy absorbing, temperature stabilizing phase change materials and methods of manufacturing same. More particularly, this invention relates to fabric coatings containing microspheres of phase change material dispersed in a polymer binder and methods of manufacturing same.

15

Background of the Invention

Coatings are typically applied to fabrics to increase water resistance, water transport, insulative ability or heat storage properties of the fabrics. Recently, microencapsulated phase change materials have been described as a suitable component for fabric coatings when exceptional heat transfer and storage capabilities are desired. In particular, International Patent Application No. PCT/US93/05119 for "Fabric with Reversible Enhanced Thermal Properties" to Colvin, et al., which is incorporated herein by reference, discloses that fabrics coated with a binder containing microcapsules filled with energy absorbing phase change material enables the fabric to exhibit extended or enhanced heat retention or storage properties.

Research has demonstrated that applying a binder containing microspheres of phase change materials with commercial coating equipment can be problematic. For example, use of solvent based gravure printing techniques in which a solvent system was employed to achieve uniform dispersion of the microspheres in a binder proved unsuccessful

because the solvent systems damaged the microspheres.

Thermoplastic gravure printing techniques also proved unsatisfactory for use with microspheres of phase change material. When using higher temperature thermoplastic gravure printing techniques, sustained temperature of 325 °F caused severe damage to the microspheres. Although lower temperature thermoplastic gravure printing techniques avoided significant damage to the microspheres, the resulting coating was found lacking in washability and durability. Moreover, lower temperature thermoplastic gravure printing techniques precluded addition of the desired amounts of the microspheres, allowing addition of microspheres of up to only about 20% by dry weight of the microsphere/binder material. This low percentage of phase change material in the coating makes the coating susceptible to undesirable heat transfer across the coating, especially in locations where phase change material is sparsely applied.

Attempts to encapsulate microspheres of phase change materials in a thermoplastic spray have also proved unsatisfactory. In particular, scattering microspheres into a stream of sprayed, fibrous thermoplastic material resulted in a binder matrix that did not fully encase the microspheres. The resulting binder/microsphere material was susceptible to loss of microspheres, which worked loose and were continually shedded from the fabric. In addition, the coating lacked uniformity of thickness and microsphere distribution.

Attempts were also made to utilize thermoplastic extrusion techniques to create a film of continuous web in which microspheres of phase change material were uniformly distributed.

However, thermal breakdown of the microspheres resulted from the higher temperatures utilized. The extrusion screw employed with these techniques also physically damaged the microspheres.

5 Phase change materials in microencapsulated form are commonly supplied as a dry powder. This powder is difficult to wet and uniformly disperse in aqueous systems. Moreover, some microencapsulated phase change materials have an internal layer of
10 modified gelatin which is hydrophilic and capable of absorbing its own weight in water. Not only does the hydrophilic quality of such microcapsules make more standard component proportions inapplicable, microcapsules which have absorbed water tend to
15 swell and associate, increasing the viscosity of the coating system above acceptable limits. Although the precise behavior of microcapsules in the coating system which have absorbed water is uncertain, it is believed that such microcapsules agglomerate,
20 reducing their dispersion throughout the binder of the coating system, which de-stabilizes the binder. This de-stabilization can increase over time. When latex binders are used with microencapsulated phase change material, de-stabilization of the latex
25 binder can continue until the latex binder coagulates.

 U.S. Patent Nos. 5,254,380, 5,211,949, 5,282,994 and 5,106,520 for "Dry Powder Mixes Comprising Phase Change Materials" describe free
30 flowing, conformable powder-like mixes of silica particles and a phase change material which the silica particles of between 7×10^{-3} to 7×10^{-2} microns are mixed with phase change material in a ratio of up to 80% by weight of phase change material. While
35 these patents describe a matrix in which microspheres of phase change materials need not be

separately encapsulated, they do not describe the use of dry powder mixes containing phase change materials in binder matrices for coating fabrics.

Research has further demonstrated that in
5 applying a binder containing microspheres of phase change materials directly to a fabric, a significant amount of binder must be applied if a high content of microencapsulated phase change material is desired. For some commercial uses, however, a
10 thick, exposed coating layer may be undesirable for the finished product.

This problem can be overcome in certain applications by insertion or lamination of the exposed coating between external sheets, substrates
15 or fabrics of the finished product. Such constructions prevent the coating from contact with the end-user or exposure to view. The finished products necessarily contain additional layer(s) of substrate, whose function is, at least in part, to
20 cover the otherwise exposed coating. In the case of a jacket lining or footwear insert, such a construction is not problematical. In other applications, however, it may be undesirable to have an additional covering layer which may needlessly
25 add weight and/or bulk to the end product.

For certain other applications, it is desirable to use highly extensible fabrics. Typically, these fabrics have an ultimate elongation at break (UE) of more than 20%. Examples of extensible fabrics
30 include knits, fabrics made from crimped or texturized yards, and fabrics made from rubber or polyurethane based yarns (such as Spandex™, made by E.I. duPont de Nemours, Co.). Garments such as stockings, undergarments, sweaters, T-shirts,
35 gloves, wet-suits, etc. must be extensible if they are to be put on easily and worn comfortably.

If a coating to be applied to an extensible fabric contains encapsulated phase change materials and has a UE much less than that of the fabric, the coating will prevent the coated fabric from stretching and making it stiff and unacceptable for use. On the other hand, if the modulus of elongation of the coating/phase change material is too high, it may make the coated fabric stiff or boardy and unsuitable for the end use.

The aforementioned problem may be solved by making a coating which is weak and has a very low UE. When such a weak coating is stretched, it breaks in many places. While this has the advantage of making the coating breathable, the product will exhibit a stiff hand until the coating is broken, after which the hand will vary from place to place on the fabric and the coating will be unsightly and may be unacceptable to consumers. In addition, the broken coating will be less resistant to wear and cleaning, pieces of the coating may break off or wear off. Finally, the portions of the stretched fabric which are no longer covered by coating will not have desired thermal properties, reducing the effectiveness of the phase change material.

It is well known that adding non-extensible particles, such as filler, reinforcements, or microencapsulated phase change materials to an elastomeric binder, reduces the UE of the composition and stiffens it. The amount of change depends principally upon the relative volumes of the filler and the elastomer, the amount of adhesion between the filler and the elastomer, and the dispersion of the filler in the elastomer. Moreover the effect of filler concentration on UE is non linear. As filler is increased, the UE falls off moderately until a concentration is reached where

the UE is reduced drastically. The concentration at which the UE falls drastically depends upon the filler (as above) and upon the elastomer.

5 In general, it appears that coatings applied under tension to fabric may result in a coated product which does not exhibit the full stretch and recovery required for the most exacting applications. In addition, it has been found then that when binders containing a 40-50% phase change
10 material content are applied by means of direct coating methods to stretch fabrics, the fabric tends to neck down before reaching the coating head and after being unrolled from the bolt upon which it is stored. The coating is then applied to the necked
15 down fabric at the coating head, after which the coating is susceptible to cracking when the fabric is later stretched during manufacture or use. Even when the coating doesn't crack, it may limit the natural stretchability of the fabric, as described
20 above.

It is against this background that the significant improvements and advancement of the present invention have taken place in the field of fabric coatings containing energy absorbing,
25 temperature stabilizing phase change materials and methods of manufacturing same.

Objects of the Invention

It is the principal object of the present invention to provide an improved fabric coating
30 composition containing phase change material of a density sufficient to effect or control heat and energy transfer across the coating and/or store heat in the coating.

It is another object of the present invention
35 to provide a coating composition of the foregoing character which will maintain substantially all of

the breathability, flexibility or other principal qualities of the fabric to which it is applied.

5 It is a further object of the present invention to provide coated fabrics having the aforementioned properties which are resistant to heat, pressure and chemicals encountered during the coating process.

10 It is a still further object of the present invention to provide coated fabrics having the aforementioned qualities which are durable, resistant to heat, moisture, solvents, laundering, and/or dry cleaning, without degradation to or loss of the phase change material.

15 It is still another object of the present invention to provide an improved method of applying coating compositions containing phase change materials and having the aforementioned qualities as coatings on fabrics by utilizing commercially available equipment.

20 It is yet another object of the present invention to provide an improved method of applying coatings containing phase change materials to fabrics without damage or degradation to the phase change materials.

25 It is still another object of the present invention to provide an improved method for evenly dispersing phase change material throughout a binder and maintaining an even distribution of the phase change material while coating a fabric with the binder and phase change material dispersion.

30 It is still another object of the present invention to develop a coating formulation and method suitable for application of a binder and phase change material composition to extensible fabrics.

35 It is a yet further object of the present invention to achieve the aforementioned objects

which producing a coated fabric which is
atheistically pleasing.

Summary of the Invention

5 The present invention comprises coatings for
fabrics and methods for manufacturing the same. A
preferred coating includes wetted microspheres
containing a phase change material dispersed
throughout a polymer latex binder, and including a
surfactant, a dispersant, an antifoam agent and a
10 thickener. Preferred phase change materials include
paraffinic hydrocarbons. To prepare a preferred
coating composition of the present invention,
microspheres containing phase change material are
dispersed in an aqueous solution of a surfactant, a
15 dispersant, and an antifoam agent mixture, followed
by dispersion in a polymer mixture to form a coating
composition. An alternative method of preparing the
coating composition of the present invention
includes dispersing microspheres containing phase
20 change material in wet cake form in an aqueous
solution of a surfactant, a dispersant, antifoam
agent and polymer to form a coating composition.
The coating composition of the present invention are
then applied as a coating on a fabric.

25 In an alternative embodiment, a substrate is
coated with an extensible binder containing
microencapsulated phase change material to form an
extensible, coated fabric. A preferred binder
contains latex and a preferred substrate is an
30 extensible fabric. The coated substrate is
optionally flocked. When the coated product is an
extensible fabric, transfer coating techniques are
preferably employed.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a section view of flocked coated substrate which is an alternate embodiment of the present invention.

5 Detailed Description of the Invention

In accordance with the present application, it has been discovered that wetting microspheres of phase change materials with water and maintaining a uniform dispersion of the microcapsules in a wet
10 coating minimizes or eliminates the tendency of such microspheres to destabilize the binder polymer in which the microspheres are dispersed.

A coating composition which includes microspheres containing a phase change material is
15 prepared by mixing dry microspheres with an excess of water to induce the microspheres to swell with water until swelling is complete. Preferably, a surfactant and a dispersant are added to the water prior to mixing with the microspheres. The
20 surfactant decreases surface tension of the layers of the microspheres and thereby promotes wetting of the microspheres. An antifoam agent is added to and mixed slowly with the microsphere/water mixture to remove air trapped as dispersed bubbles in the
25 mixture. A thickener is added to adjust the viscosity of the mixture to prevent the microspheres from floating or sinking in the mixture. A viscosity of at least 500 cps is preferred. Adjusting the pH of the mixture to 8.5 or greater
30 promotes swelling of the microspheres. Swelling is typically complete in from 6 to 24 hours, at which time the microspheres will have reached an equilibrium with the aqueous phase in which they are dispersed. Thereafter, the microsphere dispersion
35 is added to a mixture of a polymer dispersion, surfactant and dispersant having a pH approximately

the same as the pH of the microsphere dispersion. The viscosity and rheology of the resulting coating compound is adjusted to meet the requirements of the coating method employed.

5 The polymeric binder may be in the form of a solution, dispersion or emulsion in water or in organic solvent. The polymeric binder may initially be polymeric, or in the form of monomers and/or oligomers, or low molecular weight polymers which
10 upon drying and/or curing are converted to their final molecular weight and structure. These binders are preferably film-forming, elastomeric, and have a glass transition temperature in the range of about -45 °C to +45 °C, depending upon the desired
15 application. For most garment applications, an elastomeric polymer with a glass transition temperature of about -30 °C to about +12 °C is preferred.

 The polymers may be linear or branched.
20 Copolymers may be random, block or radial. The polymers may have pendant reactive groups, reactive ends or other crosslinking mechanisms, or be capable of entanglement and/or hydrogen bonding in order to increase the toughness of the finished coating
25 and/or its resistance to heat, moisture, solvents, laundering, dry-cleaning or other chemicals.

 Suitable monomers include, but are not limited to, acrylic esters (preferably alkyl-acrylates and methacrylates containing 4 to 17 carbon atoms);
30 styrene; isoprene; acrylonitrile; butadiene; vinyl acetate; vinyl chloride; vinylidene chloride; ethylene; butylene; propylene; chloroprene; etc. Polymers and copolymers based upon the above mentioned monomers and/or upon silicone; epoxy;
35 polyurethane; fluorocarbons; chlorosulfonated

polyethylene; chlorinated polyethylene; and other halogenated polyolefins are also useful.

5 The surfactant described above has a preferred wetting time of not greater than 50 seconds at a concentration of 0.10 % by the Draves Wetting Test. Nonionic and anionic surfactants are acceptable. Dioctyl sodium sulfosuccinamate (sometimes referred to herein as "DOS") is a preferred surfactant.

10 The dispersing agent employed as described above is preferably a nonionic or anionic dispersant, such as dispersants based upon phosphate esters. A 90% solution of the potassium salt of a phosphated coester of an alcohol and an aliphatic ethoxylate such as Strodex PK90™ available from
15 Dexter Chemical Company of New York City, New York is a preferred dispersant.

 From 0.1% to 0.8% by weight of dry DOS to dry microspheres and from 0.1% to 0.8% by weight of dry PK90™ to dry microspheres is effective. The total
20 amount of DOS and PK90™ is preferably apportioned equally between the dry microsphere dispersion and the polymer dispersion to which the microspheres will be added after swelling is complete.

 Suitable thickeners include polyacrylic acid,
25 cellulose esters and their derivative, polyvinyl alcohols, and others known in the art. A preferred thickener is Acrysol ASE60™ available from Rohm and Haas Company of Philadelphia, Pennsylvania. ASE60™ is preferably obtained as a 28% solution of an
30 alkali-swellaable polyacrylic acid which increases in viscosity upon neutralization. As described above, thickener is added first to achieve the desired viscosity of the microsphere dispersion, which will vary depending on the particular phase change
35 material selected, and then to adjust the wet

coating to meet the requirements of the coating method employed.

Preferred antifoam agents include aqueous dispersions of silicone oil, such as
5 polydimethylsiloxane, containing dispersed fine particle silica, and mixtures of mineral oil, surfactant and fine particle silica, such as AF 9020™ available from General Electric Company of Waterford, New York, and Advantage 831™ available
10 from Hercules Chemical Company of Wilmington, Delaware.

A preferred polymer binder is made with a dispersed polymer latex is an anionic, heat reactive, acrylic latex containing 59% non-volatiles
15 in water, such as the acrylic polymer latex marketed under the trade name Hycar XT9202™ and available from B.F. Goodrich Chemical Company of Cleveland, Ohio. The polymer latex has a glass transition temperature of -25 °C. When properly dried and
20 cured, fabric coatings made from polymer latex such as Hycar XT9202™ are washable and dry-cleanable.

The coating compositions of the present invention preferably include from 30 to 500 parts by dry weight of microspheres for each 100 parts by dry
25 weight of acrylic polymer latex. The coating compositions preferably include from 0.005% to 6% dry weight each of surfactant and dispersant to dry weight of microspheres. Water is added to total 25% to 80% of the final wet coating composition. An
30 antifoam agent of from 0% to 1% dry weight to total weight of the final wet coating composition is preferred. The most preferred ratios of components of the coating composition of the present invention are: 70 to 300 parts by dry weight of microspheres
35 for each 100 parts by dry weight of acrylic polymer latex, 0.1% to 1% dry weight each of surfactant and

dispersant to dry weight of microspheres, water totaling 40% to 60% of the final wet coating composition and antifoam agent of from 0.1% to 0.5% dry weight to total weight of the final wet coating composition.

An alternative method utilizes microspheres of phase change material which are not completely dried during the manufacturing process. Wet microspheres containing from about 25% to about 65% by weight water are preferred and can be readily handled. When using such microspheres, a surfactant and a dispersant are added to a polymer binder dispersion before the wetted microspheres are dispersed therein. DOS and Strodex PK90™ are preferably mixed with the polymer binder dispersion before the wet microspheres are mixed with and dispersed therein.

Generally speaking, phase change materials have the capability of absorbing or releasing thermal energy to reduce or eliminate heat transfer at the temperature stabilizing range of the particular temperature stabilizing material. The phase change material inhibits or stops the flow of thermal energy through the coating during the time the phase change material is absorbing or releasing heat, typically during the material's change of phase. This action is transient, i.e., it will be effective as a barrier to thermal energy until the total latent heat of the temperature stabilizing material is absorbed or released during the heating or cooling process. Thermal energy may be stored or removed from the phase change material, and can effectively be recharged by a source of heat or cold. By selecting an appropriate phase change material, a fabric can be coated for use in a particular application where the stabilization of temperatures is desired. Two or more different phase change

materials can be used to address particular temperature ranges and such materials can be mixed.

Paraffinic hydrocarbon phase change materials suitable for incorporation into fabric coatings are shown below in Table I. The number of carbon atoms contained in such materials and is directly related to the melting point of such materials.

TABLE I

	COMPOUND	NO. CARBON ATOMS	MELTING POINT °C
10	n-Octacosane	28	61.4
	n-Heptacosane	27	59.0
	n-Hexacosane	26	56.4
	n-Pentacosane	25	53.7
	n-Tetracosane	24	50.9
15	n-Tricosane	23	47.6
	n-Docosane	22	44.4
	n-Heneicosane	21	40.5
	n-Eicosane	20	36.8
	n-Nonadecane	19	32.1
20	n-Octadecane	18	28.2
	n-Heptadecane	17	22.0
	n-Hexadecane	16	18.2
	n-Pentadecane	15	10.0
	n-Tetradecane	14	5.9
25	n-Tridecane	13	-5.5

Phase change materials such as the listed paraffinic hydrocarbons are preferably formed into microspheres and encapsulated in a single or multi-layer shell of gelatin or other materials.

Encapsulated microsphere diameters of from 1 to 100 microns are preferred, most preferably in the range 10 to 60 microns. Encapsulated microspheres

containing phase change materials are sometimes referred to herein as "microPCMs." Microspheres may also be bound in a silica matrix of sub-micron diameters. Microspheres containing n-octadecane or n-eicosane are suitable for fabric coatings for clothing. Such microspheres are available from MacGill Enterprises, Inc. of West Milton, Ohio and Microtek Laboratories, Inc. of Dayton, Ohio.

EXAMPLE I

A preferred coating formulation where high phase change material content and limited extensibility is required, for example with non- or low-stretch fabrics such as non-woven or woven fabrics, is prepared as shown in Table II.

TABLE II

COMPONENT	WT %	DIRECTIONS
MICROSPHERE DISPERSION:		
Water	35.00	
75% DOS	0.40	
Strodex PK90 (90% NV)	0.20	
n-Eicosane microspheres (dry)	36.50	
Acrysol ASE60 (28% NV)	1.00	Mix, dispersing ingredients well.
AF9020 (20% NV)	0.05	Mix slowly with dispersed ingredients until foam dissipates.
Ammonium hydroxide (28%)	0.50	Add slowly to the defoamed dispersion, with good mixing.
		Let stand 6 hours. Remix immediately before use.
POLYMER BINDER DISPERSION:		
Hycar XT9202 latex polymer	21.35	
75% DOS	0.20	
Strodex PK90	0.10	

Acrysol ASE60 (28% NV)	3.40	
Hercules Advantage 831	0.30	Mix ingredients slowly until foam dissipates.
COATING:		
Ammonium Hydroxide	1.00	Slowly add Microsphere Dispersion to Polymer Binder Dispersion; add ammonium hydroxide slowly with good mixing thereto.

5

EXAMPLE II

An alternative coating formulation where high phase change material content and limited extensibility is required, for example with non- or low-stretch fabrics such as non-woven or woven fabrics, is prepared as shown in Table III.

10

TABLE III

COMPONENT	WT %	DIRECTIONS
Hycar XT9202	21.00	
75% DOS	0.40	
Strodx PK90 (90% NV)	0.33	Mix.
50% wet n-Octadecane microspheres	72.00	Add slowly to latex polymer mixture, with good mixing, dispersing microspheres well.
Acrysol ASE60 (28% NV)	4.40	
AF9020 (20% NV)	0.05	
Hercules Advantage 831	0.30	Mix ingredients slowly until foam dissipates.
Ammonium Hydroxide (28%)	1.52	Add slowly, with good mixing.

15

20

25

Addition of microspheres as described above in the preferred weight ratios eliminates tack and prevents blocking of the coated fabrics typically experienced with coatings having low glass transition temperature polymers such as those based on acrylic latex polymers. Tack, the tendency of material to stick to itself, can make rolls of

coated fabric difficult to unroll. This can occur when rolls of coated fabric are stored in warm places or are stored under pressure of rolls stacked on top of one another. Antiblocking additives are typically added to coating formulations to prevent tack. The presence of microspheres in the coatings of the present invention eliminates the need for antiblocking additives.

Non-foam coating compositions like those described in Examples I and II above are suitable for application to substantially non-extensible fabrics of both woven and non-woven construction. A preferred coated fabric is produced using the non-foam coating like that of Example I and a 100% polyester, non-woven fabric having a weight of 0.8 oz/sq yd. A preferred fabric selected is HEF™ (a hydro-entangled fiber) obtained from Veretec™ of Bethune, South Carolina. Similar fabrics are available from duPont de Nemours Company. Using a wet coating composition containing 50% by dry weight of microspheres, a knife-over-roll coating head configuration is employed. A desired weight of 2.5 oz dry weight of microspheres/sq yd is obtained with a knife-over roll gap of 0.022 inches off the fabric. The coating line speed is 8 linear yards per minute. The coating is cured at a temperature of approximately 260 °F.

EXAMPLE III

A preferred foam coating formulation of the present invention may be used with breathable fabric to maintain the heat and moisture dissipation capability of the fabric. In this example, the materials are subject to mechanical frothing. Foam stabilizers are added to maintain the foam after application to the fabric. Foam stabilizers may be inorganic salts of fatty acids or their sulfate

partial esters, anionic surfactants, among other compounds. Preferred foam stabilizers for use with phase change material microspheres are sodium lauryl sulfate, ammonium stearate, di-sodium-n-octadecyl sulfosuccinamate and mixtures thereof. Ammonium stearate concentrations (dry as a percent of wet coating) of 0.5% to 6% plus 0.2% to 4% sulfosuccinamate are most preferred. The coatings are prepared as shown in Table IV.

TABLE IV

COMPONENT	WT %	DIRECTIONS
Water	4.69	
75% DOS	0.20	
Strodex PK90 (90% NV)	0.17	
Hycar XT9202	33.74	
35% wet n-Octadecane microspheres	54.53	Add slowly to above ingredients, dispersing microspheres well.
AF9020 (20% NV)	0.05	Mix slowly, until foam dissipates.
Acrysol ASE60 (20% NV)	1.55	
Hercules Advantage 831 (28% NV)	0.23	Mix ingredients slowly until foam dissipates.
Ammonium Hydroxide (28%)	0.60	Add slowly while mixing. Do not mix in air.
Ammonium Stearate (33%)	2.96	
Di-sodium-n-octadecyl-sulfosuccinamate (35%)	1.28	Add slowly, with good mixing.

Preferred foam coatings contain ammonium stearate in an amount by dry weight of from 0.25% to 10% of the total weight of the final wet coating composition foam is preferred and from 0.1 to 8% dry weight of sulfosuccinamate to total weight of the final wet coating composition foam. Most preferably, ammonium stearate by dry weight 1% to 3% of the total weight of the final wet coating

composition foam and the sulfosuccinamate by dry weight comprises from 0.3 to 2% dry weight to total weight of the final wet coating composition foam.

5 The liquid coating is mechanically foamed by pumping through an Oakes mixer or similar mechanical foamer. The mixer injects air into the liquid and finely disperse the air. The foamed liquid is pumped to a coating head, usually a knife coater, where it is spread onto the fabric. The fabric/foam
10 coating is then passed through a heated oven to dry and cure the foam.

 Foam coating compositions like those described in Example III are also suitable for application to substantially non-extensible fabrics of both woven
15 and non-woven construction when maintaining breathability of the fabric is desired. A preferred methodology includes applying the foam coating of Example III to HEF™ having a weight of 1½ oz/sq yd. The wet coating composition of Example III is foamed
20 to a preferred blow ratio of air to wet compound of 2:1, with acceptable blow ratios ranging from ½:1 to 10:1. A knife-over-roll coating head configuration is employed. The desired weight of 0.5 oz dry weight of microspheres/sq yd is obtained with a
25 knife-over roll gap of 0.018 inches off the fabric. The fabric is drawn through the coating line at a rate of 10 linear yards per minute. The coating is cured at a temperature of approximately 260 °F, with the fabric carried on a tenter frame to prevent
30 shrinkage of the fabric.

EXAMPLE IV

 Tests were conducted on acrylic fleeces in which the fibers containing microPCMs, and on non-woven materials (sometimes referred to herein as
35 "substrate") having a coating containing microPCMs. Acrylic fleeces without microPCMs having

approximately the same weight per unit area as the fleeces with microPCMs, and substrates without microPCMs having the same thickness as the non-woven substrates having a coating containing microPCMs, served as comparison materials. Specific data regarding the sample materials tested are included in Table V.

TABLE V

Materials Tested	Acrylic with PCM	Acrylic without PCM	Substrate with PCM	Substrate without PCM
Wt/unit area (g/m ²)	270	250	227	207
Stand thickness (mm)	5.40	5.63	0.63	0.61
Compressibility (lbs)	12	16	13	20
Raw density (kg/m ³)	49	44	360	339

The content of microPCM in the acrylic fleeces was approximately 10 per cent. About 7 g/m² microPCM was included in the coating of the non-woven substrate. This is equal to a content of microPCM of about 3%. The phase change temperature of the microPCM material ranged from about 22° C to about 25° C.

Tests of water-vapor permeability and water-vapor absorption of the materials were based upon the test methods of the standards DIN 53 332 and DIN 53 333. The tests of the water-vapor permeability were carried out under constant climatic conditions of 23 °C temperature and 40% relative humidity. The water-vapor absorption of the materials was tested at a constant environmental temperature of 23 °C at varying relative humidities. The following thermophysical parameters of the materials were measured: thermal conductivity (A);

thermal resistance (R); temperature conductivity (a); and specific thermal capacity (c).

Test results indicated that the water-vapor permeability is not influenced by the incorporation of microPCMs. The acrylic fleeces tested possess a water-vapor permeability of about 5 mg/cm²/h as a result of the material structure. The non-woven substrate to which the microPCM layer is applied is with about 0.75 mg/cm²/h, nearly impermeable for water-vapor.

The water-vapor absorption of the samples is primarily determined by the absorption ability of the basic material. The incorporated microPCM causes a slight increase of the water-vapor absorption under the same climatic conditions. The water-vapor absorption of the acrylic fleece without microPCM was about 1.5% at a temperature of 23 °C and a relative humidity of 80%. The acrylic fleece with microPCM absorbs about 0.3% more water-vapor under the same conditions.

Tests of heat insulation and the heat storage were carried out under varying temperature, humidity and static pressure. Test conditions with a material temperature in the phase change range of 24 °C, a material humidity that results from 30% air humidity and a pressure of 1 kPa were selected as a starting point for the measurements. Table VI is a summary of the test results.

TABLE VI

thermophysical parameters	Acrylic with PCM	Acrylic without PCM	Substrate with PCM	Substrate without PCM
A (w/m K)	0.0398	0.0342	0.1012	0.1782
R (m ² K/W)	0.1281	0.1491	0.0057	0.0029
c (kJ/kg K)	3.022	2.391	2.468	1.840

As shown above in Table VI, materials with incorporated microPCM possess an essentially higher heat storage than the comparison material. The heat insulation of the compact non-woven substrate is enhanced by the microPCM coating. The heat insulation of the acrylic fleece is mainly determined by the air enclosed in the material as a result of the dispersed structure of the fabric.

It has been determined that the heat insulation properties of the materials containing microPCM remain nearly constant in the temperature range of the specific phase change, in contrast to the behavior of materials which do not contain microPCM. The variation of the heat insulation of the materials with microPCM is essentially lower contrary to the comparison material in changes of material humidity. The materials with microPCM possess when raising the pressure on the textile a lower decrease in the heat insulation than the comparison material due to a lower compressibility of the materials with microPCM.

To determine the protection effect of the samples, the samples were brought in contact with a 70 °C tempered plate after cooling under the phase change temperature. The time required to reach a temperature equivalent to the pain threshold of the human skin on back of the sample was determined. The higher protection effect for the materials with microPCM was confirmed.

EXAMPLE V

A preferred coating formulation in situations where a medium level of phase change material content is desired and high extensibility must be maintained, for example with medium- or high-stretch fabrics such as melt blown polyester

stretchable fabrics, knit fabrics, including warp knit fabrics, is prepared as shown in Table VII.

TABLE VII

	COMPONENT	WT %	DIRECTIONS
5	MICROSPHERE DISPERSION:		
	Water	21.54	
	75% DOS	00.80	
	Strodex PK90 (Dexter Chemical; 90% NV)	00.40	
10	Polyoxyethylene 20POE oleyl ether 20% NV	2.10	
	Dry beads containing octadecane	17.80	
	Acrysol ASE60 28% NV	00.60	disperse above ingredients well
15	AF9020	00.10	mix slowly until foam dissipates then add slowly w/good mixing
	Ammonium Hydroxide (28%)	1.00	let stand for 6 hours, remix immediately before use
	POLYMER BINDER DISPERSION:		
20	Low Ammonia Natural Latex 62% NV	38.50	
	10% Potassium Hydroxide	2.00	
	Water	3.46	
	Ammonium Cascinate 15% NV	2.00	
25	Polyoxyethylene 20 oleyl ether 20% NV	2.00	
	Zinc Oxide dispersion 50% NV	1.50	
	Zinc di-n-butylidithiocarbamate dispersion 50% NV	1.00	
30	AF 9020 (General Electric Co.; 20% NV)	00.10	
	Ammonium Hydroxide (28%)	2.00	mix polymer binder dispersion; slowly add microsphere dispersion polymer binder dispersion with good mixing;
	Acrysol ASE60 28% NV	3.00	add slowly with good mixing;

Application of the coating composition of Example V by direct coating methods, for example, by spray coating, produces generally unsatisfactory results. However, it has been discovered that

5 transfer coating the coating composition of Example V using knife-over-roll technique to release paper for subsequent transfer to a fabric of medium extensibility produces a satisfactory coated fabric. In one embodiment, the coating formulation of

10 Example V, which is referred to herein as a stretchable, breathable ("SB") coating composition, was applied using knife-over-roll technique to a substantially rigid transfer paper at a loading rate which, after curing, obtained a loading rate of 2.5

15 oz. of encapsulated phase change material per square yard. After passing through the coating head, Demique®, an extensible fabric manufactured by Kimberly-Clark Company, was applied to the uncured coating on the coated release paper in a relatively

20 tensionless state. The fabric was then bonded to the composition on the coated release paper by application of slight pressure as it passed through a nip roll assembly. The resulting fabric/coating paper structure was then fed through a curing oven,

25 after which the release paper was stripped from the product leaving the Demique® fabric in an evenly coated state.

By so keeping the Demique® fabric in a nearly tensionless state, maximal extensibility and

30 recovery were maintained after coating. In addition, the microsphere/binder coating was prevented from significantly penetrating the structure of the elastic fabric, thereby maximally maintaining the elasticity of the fabric. In

35 general, application of the microsphere/binder dispersion to the stretch fabric using the above

described transfer coating process, allowed for a controlled application of the coating to the stretch fabric without excessively penetrating the fabric, in a manner not heretofore achieved using spray coating technology.

Referring now to Fig. 1, in an alternate embodiment of the coated fabric 10 of the present invention, a SB binder 12 containing a 40% by weight content of encapsulated phase change materials 14 in the wet dispersion state is foamed, (i.e. whipped with air), to create a cellular coating 16 through which moisture vapor passes in the finished product. The coating 16 which results is referred to as a stretchable/breathable/foam (hereinafter "SBF"), and is preferably applied to a release paper (not shown) using knife-over-roll technique. The preferred loading level for the microencapsulated phase change material 14 is approximately 1½ oz. per square yard. Before the SBF coating 16 is cured, precision cut nylon fibers 18 are electrostatically charged and dropped onto a surface 20 of the uncured coating 16. The charged fibers 18 stand on end upon penetrating the coating 16 and are cured in this state, to produce a flocked coating 22 on the release paper (not shown). The release paper is removed from the flocked coating 22 and the flocked coating 22 is then applied with either heat or adhesive to an extensible fabric 24. This results in a binder/phase change material coating 16 sandwiched between the extensible fabric 24 and the flocked fibers 18. The flocking 18 adds very little weight to the finished product 10, yet gives it a velvet like appearance and feel, with the coating 16 especially useful for products requiring a high moisture vapor transmission rate, commonly referred to as breathable fabrics.

In another embodiment of the present invention, a release paper is coated with a layer of a SBF having a 40% by weight content of an encapsulated phase change material applied using transfer coating methodology to a release paper to obtain a 1½ oz. per square yard finished weight of microencapsulated phase change material. One layer of this coating is transferred in an uncured state to a stretch fabric, for example, the Demique® fabric identified above, and the release paper removed. This coated fabric is referred to herein as a facing ply. Another layer of the coating is maintained on the release paper, flocked as described above, and cured. This flocked coating layer is referred to in here as a backing ply. The backing ply is then applied to the facing ply, with the microsphere/binder dispersion of the backing ply and of the facing ply bonded together. The resulting product has a medium to high content of phase change material of 2½ oz. per square yard but does not have exposed, tacky coating surfaces which might otherwise cause the finished product to block or adhere to itself.

Another embodiment of the present invention comprises two opposing flocked coating layers, each layer containing microencapsulated phase change materials dispersed throughout. In this embodiment, a binder/microsphere dispersion such as that described in Example V is applied to release paper to obtain a dispersion of 1½ oz. per square yard of coating. The coating is then flocked as described above. Thereafter, release paper is removed from two sheets of identically sized coating, and the exposed coatings of each sheet are bonded together, thereby adhering each coating layer to an opposed and identical coating layer. The resulting product is a double-sided flocked material which is stable

and easy to handle. Such a product is an ideal lamination substrate for use in multi-fabric applications.

5 In yet another embodiment of the present invention, a binder containing encapsulated phase change materials is coated to a leather substrate. A preferred encapsulated phase change material is a paraffinic hydrocarbon consisting essentially of octadecane which may be dispersed throughout an
10 acrylic binder. Such a coated leather may be employed in the leather uppers of boots, with the coating layer facing and contacting the foot of the wearer.

15 Presently preferred embodiments of the present invention and many of its improvements have been described with a degree of particularity. It should be understood that this description has been made by way of preferred examples, and that the invention is defined by the scope of the following claims.

What is claimed is:

1. A wet coating composition for fabrics,
comprising:

100 parts dry weight of a polymer binder;

5 30 to 500 parts by dry weight of microspheres
containing a phase change material for each 100
parts dry weight of said polymer binder;

0.001% to 6% dry weight of a surfactant to dry
weight of said microspheres;

10 0.001% to 6% dry weight of a dispersant to dry
weight of said microspheres;

25% to 80% by weight water of the total weight
of the wet coating composition; and

15 0% to 1% by weight of dry antifoam agent to the
total weight of the wet coating composition.

2. The coating of claim 1 wherein said phase
change material is a paraffinic hydrocarbon.

3. The coating of claim 2 wherein said binder
polymer is an anionic acrylic latex polymer, said
20 microspheres are from 70 to 300 parts by dry weight
of said polymer latex and said water is from 40% to
60% of the total weight of the wet coating
composition.

4. The coating of claim 2 wherein said binder
25 polymer is film-forming, elastomeric and has a glass
transition temperature in the range of about -45 °C
to +45 °C.

5. The coating of claim 2 wherein said binder
polymer is film-forming, elastomeric and has a glass
30 transition temperature in the range of about -30 °C
to about +12 °C.

6. The coating of claim 2 wherein said binder
polymer is comprised of monomers selected from the
group consisting of acrylic eaters, styrene,
35 isoprene, acrylonitrile, butadiene, vinyl acetate,

vinyl chloride, vinylidene chloride, ethylene, butylene, propylene and chloroprene.

7. The coating of claim 2 wherein said binder polymer is selected from the group consisting of
5 silicone, epoxy, polyurethane, fluorocarbons, chlorosulfonated polyethylene and chlorinated polyethylene.

8. The coating of claim 5 wherein the dry weight ratio of said dispersant to dry weight of
10 said microspheres is from 0.1 to 1%

9. The coating of claim 5 wherein the dry weight ratio of said surfactant to dry weight of said microspheres is from 0.1 to 1%

10. The coating of claim 1 wherein the phase
15 change material is a paraffinic hydrocarbon.

11. The coating of claim 10 wherein the polymer is an anionic acrylic latex polymer, the microspheres are from 70 to 300 parts by dry weight of the polymer latex and the water is from 40% to
20 60% of the total weight of the wet coating composition.

12. The coating of claim 11 further comprising:

0.3% to 18% by dry weight of a foam stabilizing
25 agent selected from the group consisting of inorganic salts of fatty acids, sulfate partial esters of inorganic salts of fatty acids, anionic surfactants, and mixtures thereof, to the total weight of the wet coating composition.

13. The coating of claim 11 further comprising:

0.3% to 18% by dry weight of a foam stabilizing agent selected from the group consisting of sodium lauryl sulfate, ammonium stearate, di-sodium-n-
35 octadecyl sulfosuccinamate and mixtures thereof, to the total weight of the wet coating composition.

14. The coating of claim 11 further comprising:

0.2% to 10% by weight of dry ammonium stearate to the total weight of the wet coating composition; and

0.1% to 8% by weight of dry di-sodium-n-octadecyl-sulfosuccinamate.

15. The coating of claim 11 further comprising:

1% to 3% by weight of dry ammonium stearate to the total weight of the wet coating composition; and

0.3% to 2% by weight of dry di-sodium-n-octadecyl-sulfosuccinamate.

16. A method of manufacturing a coated composition for a substantially non-extensible fabric comprising the steps of:

mixing water, a surfactant, a dispersant, microspheres containing a phase change material, and a thickener to produce a microsphere mixture;

dispersing said microspheres throughout said microsphere mixture to produce a microsphere dispersion;

adding an antifoam agent to said microsphere dispersion to dissipate foam from said microsphere dispersion;

mixing a latex polymer, a surfactant, a dispersant, a thickener and an antifoam agent to form a polymer binder dispersion; and

mixing said polymer binder dispersion with said microsphere dispersion to produce the coating composition.

17. The method of claim 16 further comprising the steps of:

adjusting the pH of said microsphere dispersion by addition of a base prior to mixing said

microsphere dispersion with said polymer binder dispersion; and

adjusting the pH of said coating composition by addition of a base after mixing said microsphere dispersion with said poly binder dispersion.

18. The method of claim 16 further comprising the step of:

maintaining said microspheres in said microsphere dispersion for from 1 to 48 hours prior to mixing said polymer binder dispersion with said microsphere dispersion to produce the coating composition.

19. The method of claim 16 further comprising the step of:

maintaining said microspheres in said microsphere dispersion for from 6 to 24 hours prior to mixing said polymer binder dispersion with said microsphere dispersion to produce the coating composition.

20. A method of manufacturing a coating composition comprising the steps of:

mixing a latex polymer, a surfactant and a dispersant;

adding microspheres containing a phase change material and at least 25% by weight of water to the latex polymer mixture to obtain a microsphere/latex mixture;

dispersing the microspheres throughout the microsphere/latex mixture to obtain a microsphere/latex dispersion;

mixing the microsphere/latex dispersion with an antifoam agent and a thickener to defoam and thicken the microsphere/latex dispersion; and

adjusting the pH of the defoam and thickened microsphere/latex dispersion to create the coating composition.

21. An extensible material, comprising:
an extensible fabric;
an extensible binder bonded to said fabric; and
microspheres containing a phase change material
5 dispersed in said binder.

22. The extensible material of claim 21
wherein said phase change material is a paraffinic
hydrocarbon.

23. The extensible material of claim 22
10 further comprising:

a plurality of fibers mounted in said binder
and extending away from said extensible fabric.

24. The extensible material of claim 22
wherein said binder comprises a latex material.

25. The extensible material of claim 24
15 further comprising:

a plurality of fibers mounted in said latex
binder and extending away from said extensible
fabric.

26. The extensible material of claim 22
20 wherein said binder and said phase change materials
weigh collectively from approximately $1\frac{1}{4}$ to
approximately $2\frac{1}{2}$ ounces per square yard.

27. The extensible material of claim 23
25 wherein said binder and said phase change materials
weigh collectively from approximately $1\frac{1}{4}$ to
approximately $2\frac{1}{2}$ ounces per square yard.

28. The extensible material of claim 24
wherein said binder and said phase change materials
30 weigh collectively from approximately $1\frac{1}{4}$ to
approximately $2\frac{1}{2}$ ounces per square yard.

29. The extensible material of claim 25
wherein said binder and said phase change materials
weigh collectively from approximately $1\frac{1}{4}$ to
35 approximately $2\frac{1}{2}$ ounces per square yard.

30. A method of manufacturing a coated composition for an extensible fabric comprising the steps of:

5 mixing a plurality of microspheres containing a phase change material with an extensible binder to form a coating composition;

applying said coating composition to a release paper to produce a coated paper having an exposed coating and an opposed paper surface;

10 bonding said exposed coating of said coated paper to an extensible fabric to form a fabric, coating and paper laminate; and

removing said release paper from said laminate to produce an extensible, coated material.

15 31. The method of claim 30 further comprising the step of:

foaming said extensible binder.

32. The method of claim 31 further comprising the step of:

20 curing said binder after removal of the release paper removal step.

33. The method of claim 32 wherein the binder comprises a latex.

25 34. A method of manufacturing a coated composition for a substrate comprising the steps of:

mixing a plurality of microspheres containing a phase change material with a binder to form a coating composition;

30 applying said coating composition to a release paper to produce a release paper coating have an exposed coating surface and an opposing paper contact surface;

35 mounting a plurality of fibers in said exposed coating surface to produce a flocked surface of said release paper coating which is opposite said paper contact surface;

removing said release paper from said flocked coating to expose said paper contact surface; and bonding said paper contact surface of said flocked coating to said substrate to form a flocked product containing a phase change material.

35. The method of claim 34 wherein said substrate is a fabric.

36. The method of claim 34 wherein said substrate is extensible.

37. The method of claim 35 wherein said fabric is extensible.

38. The method of claim 34 wherein said substrate is leather.

39. The method of claim 34 wherein said flocked produced contains approximately $1\frac{1}{4}$ to approximately $2\frac{1}{2}$ ounces of said coating composition per square yard.

40. The method of claim 37 wherein said flocked produced contains approximately $1\frac{1}{4}$ to approximately $2\frac{1}{2}$ ounces of said coating composition per square yard.

1/1

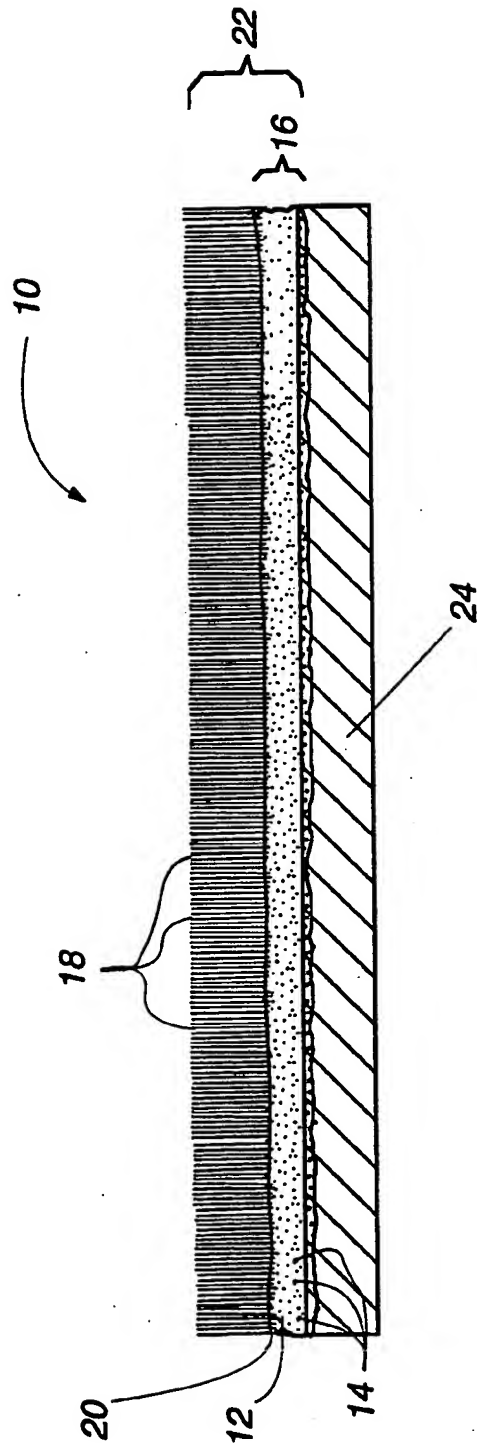


Fig. 1

SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/07467

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C09K 3/18; 3/20; B32B 19/04.

US CL :252/70; 523/402; 427/443.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,939,020 (TAKASHIMA et al.) 03 JULY 1990, see entire document.	1
--		-----
Y		2-40
Y, P	US, A, 5,366,801 (BRYANT et al.) 22 NOVEMBER 1994, see entire document.	1-40
Y	US, A, 4,006,273 (WOLINSKI et al.) 01 FEBRUARY 1977, see entire document.	1-40
A	US, A, 4,747,240 (VOISINET et al.) 31 MAY 1988, see entire document.	1-15
A	US, A, 4,935,294 (MISEVICH et al.) 19 JUNE 1990, see entire document.	1-40

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

Z

document member of the same patent family

Date of the actual completion of the international search

21 SEPTEMBER 1995

Date of mailing of the international search report

19 OCT 1995

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

RICHARD JONES aco

Telephone No. (703) 308-1235